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# DIAMONDLIKE CARBON PROTECTIVE COATINGS FOR IR MATERIALS

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## ABSTRACT

Diamondlike carbon (DLC) films have the potential to protect optical windows in applications where it is important to maintain the integrity of the specular transmittance of the window. Ion beam deposition methods have been found to be useful for the application of these films on ZnS and ZnSe infrared transmitting windows. The films must be adherent and durable such that they protect the windows from rain and particle erosion as well as chemical attack. In order to optimize the performance of these films, 0.1 μm thick diamondlike carbon films were deposited on fused silica and silicon wafers, using three different methods of ion beam deposition. One method was sputter deposition from a carbon target using an 8 cm ion source. The merits of hydrogen addition were experimentally evaluated in conjunction with this method. The second method used a 30 cm hollow cathode ion source with hydrocarbon/Argon gases to deposit diamondlike carbon films from the primary beam at 90 to 250 eV. The third method used a dual beam system employing a hydrocarbon/Argon 30 cm ion source and an 8 cm ion source. Films were evaluated for adherence, intrinsic stress, infrared transmittance between 2.5 and 50 μm, and protection from particle erosion. An erosion test using a sandblaster was used to give quantitative values of the protection afforded to the fused silica by the diamondlike carbon films. The fused silica surfaces protected by diamondlike carbon films were exposed to 100 μm diameter $SiO_2$ particles at 60 mi/hr

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(26.8 m/sec) in the sandblaster. The protective quality of the films was characterized by a change in the specular transmittance, evaluated at a wavelength of 632.8 nm using a neon-helium laser ellipsometer. These measurements indicate that the diamondlike carbon films do protect the fused silica.

## INTRODUCTION

Zinc sulfide (ZnS) and zinc selenide (ZnSe) are two of the most widely used broadband, infrared-transparent optical materials. These and most other long wavelength optical windows are soft and undergo serious degradation when subjected to severe environmental conditions such as sand or rain impact. This has led to attempts to develop new materials with improved properties, that harden these infrared windows. Hard thin films can also be used to protect these windows from impact.

Diamondlike carbon (DLC) films have the potential to protect the optical integrity of these windows (Refs. 1 and 2). These films are transparent over a broad spectral range, resist chemical attack by acids and bases, and are moisture and abrasion resistant (Ref. 3), making them ideally suited as protective surfaces. The desired films must be adherent and durable such that they protect ZnSe and ZnS windows from rain and particle erosion as well as chemical attack. A low film stress level is also desirable to allow deposition of thick hard films for maximum protection on the soft ZnSe and ZnS materials. Since ZnS and ZnSe are very expensive, DLC films, 0.1 μm thick, were first deposited in a preliminary fashion on fused silica and silicon substrates to evaluate deposition methods. Three different methods of ion beam deposition were used to generate the films. These films were then evaluated for adherence, intrinsic stress, infrared transmittance, and protection from particle erosion. An erosion test (Ref. 4) using a sandblaster was developed to give quantitative values of the protection the diamondlike films afforded

to the fused silica. The erosion test along with the infrared transmittance, adhesion, and intrinsic stress measurements were used to evaluate the three ion beam deposition methods. The results of these studies are presented in this paper.

## ION SOURCE AND DEPOSITION PROCEDURE

Three different ion source systems were used to generate DLC films; ion beam sputter deposition from a carbon target (Ref. 5), and ion beam deposition via hydrocarbon decomposition using both single and dual ion beam systems (Refs. 3 and 6). DLC films formed by ion beam sputter deposition from a graphite target is described by Banks and Rutledge in Ref. 5. In conjunction with this method, hydrogen gas was introduced in the vacuum chamber to evaluate the effect of hydrogen addition to these films. The introduction of hydrogen raised the background pressure from $5x10^{-5}$ to $7\text{-}10x10^{-5}$ torr. The ion source, using argon gas, directed a beam of 1000 eV ions at an average current density of 1 $mA/cm^2$ at the graphite target.

Both the single and dual beam systems (Fig. 1) using hydrocarbon gases are described in detail in Refs. 3 and 6. Minimum molar ratios of hydrocarbon to argon gases needed to deposit diamondlike films were 0.28 for $CH_4$ to argon, and 0.10 for $C_4H_{10}$. No films were observed at lower hydrocarbon to argon ratios since this condition did not allow a net deposition of C atoms due to the more dominant sputtering effect of the Ar ions. Films were deposited at argon ion energies ranging from 90 to 250 eV.

The 8 cm ion source was used during dual beam deposition to direct a beam of energetic (200 to 600 eV) argon ions at a current density of 25 $\mu A/cm^2$ on the substrates while the deposition from the 30-cm ion source was taking place. When the ion energy of this second beam was greater than 600 eV, no net film formation was found. The beams were approximately monoenergetic and no mass selection was attempted.

The films presented in this paper were deposited on either fused silica or silicon substrates. Before the deposition process was allowed to take place the substrates were precleaned using the ion source (at ~500 to 1000 eV) to remove contaminants and trapped gases.

## RESULTS AND DISCUSSION

### Erosion Tests

An erosion test was developed (Ref. 4), using a sandblaster, to give quantitative values of the protection afforded to the fused silica by the DLC films. DLC protected fused silica and unprotected fused silica surfaces were exposed to 100 μm diameter $SiO_2$ particles at 60 mi/hr (26.8 m/sec) in sand erosion tests. The protective quality of the films was characterized by the resulting change in the specular transmittance, evaluated at 632.8 nm using a neon-helium laser ellipsometer (Ref. 4).

Two-by-two centimeter fused silica samples were half coated with DLC film and then placed in the sandblaster. Only half of the fused silica and half of the DLC deposited coating were then exposed to the $SiO_2$ particles for various periods of time; the other half of the fused silica sample was protected from erosion by using kapton tape as protection. Thus, the resulting four quarters of the sample were: fused silica, eroded fused silica, DLC film and eroded DLC film. The normalized specular transmittance (exposed/unexposed) of both a coated fused silica sample with a 0.10 μm thick DLC film and uncoated fused silica sample plotted as a function of exposure time in the erosion test are shown in Fig. 2. The data were normalized to eliminate experimental errors in the erosion tests and the optical measurements. This normalization allows for better evaluation of the data at the lower exposure times where the transmittance is still high (greater than 80 percent). This normalization however, does not allow the two curves to meet at large exposure times, because there is optical absorption in the film at 632.8 nm and hence at $t = \infty$ the two

curves differ by the ratio of the transmittance of the film. The data in Fig. 2 suggest that the fused silica protected with a DLC film 0.10 μm thick would extend lifetime when compared to unprotected fused silica. It should be noted that the fused silica substrates used in these tests were not very good under conditions of tensile stress, for in adherence tests a force of only 30 psi could remove an area of fused silica from the rest of the substrate. Thus it is felt that the protection afforded by the DLC films might be greater than those indicated by these tests. Because of the uncertainty in the various parameters (pressure, time, particle velocity, particle integrity, etc.) involved in the erosion tests, the data in Fig. 2 is presented in Fig. 3 in a manner that eliminates the exposure time and highlights the protection afforded by the DLC films. Shown in Fig. 3 is the normalized specular transmittance of DLC protected fused silica versus the normalized specular transmittance of uncoated fused silica after exposure to the erosion test. The dashed line with a slope of one is that of unprotected fused silica. Also shown are fused silica samples protected with 0.1 and 0.2 μm thick DL film protected fused silica samples made using $CH_4$ in the single beam ion source. It is clear that a 0.2 μm DLC film extends erosion lifetime more than a 0.1 μm DL film.

Figure 4, plotted in a manner similar to Fig. 3, shows the effect of ion beam deposition method on protection. All DLC films presented in this figure are 0.1 μm thick. The DLC films generated using sputter deposition of a carbon target, and deposition of $CH_4$ using either a single or dual ion beam system do protect the fused silica and appear to be independent of the deposition method. Data on sputter deposited films with hydrogen added are also presented in Fig. 4. These hydrogen impregnated films erode at a rate faster than unprotected fused silica, possibly because they may be almost polymeric due to their easy access to hydrogen bonding.

The eroded surfaces were viewed with both a scanning electron microscope and an optical microscope to find erosion patterns. The roughness of the surface was determined by using a Tencor α-Step profilometer. The surface roughness of the DLC film portion of the fused silica samples was much less than that of the uncoated region. The impact of the $SiO_2$ particles causes a slight increase in surface elevation of the unprotected fused silica at the sites of the crater edges (Ref. 4). For the fused silica portion protected with DLC film there is an absence of sites of surface elevation, and also a decrease in the number of craters formed.

## Infrared Transmittance

A Perkin Elmer infrared (IR) spectrophotometer was used to measure the IR transmittance of DLC films deposited on Si and ZnSe substrates. Shown in Fig. 5 is the spectral transmittance of a 0.1 μm DL film deposited on ZnSe measured between 2.5 and 25 μm. The film was deposited using $CH_4$ in the single beam ion source. The DLC film did not change the spectral transmittance in this wavelength region.

DLC films deposited on Si substrates acted as antireflective coatings, causing an enhancement in the transmittance that was greatest at shorter wavelengths and decreased with increasing wavelength. This antireflective property was observed for all DLC films deposited on Si, was independent of deposition method, and is shown in Table I as a percentage increase in transmittance at 5 and 10 μm. Since the films were prepared primarily for erosion tests, they were too thin to observe the classic C-H absorption bands in the 3.3 to 3.4 μm region.

## Film Hydrogen Content

Nuclear reaction analysis for hydrogen was performed by bombarding the films with $N^+$ ions (Ref. 7). Details of this technique are described by Lanford (Ref. 8) and Ziegler et al. (Ref. 9). This technique was used by

Angus et al. (Ref. 7) to show that DLC films made with various ion beam deposition methods have very similar hydrogen depth profiles. The atomic ratio of hydrogen to carbon (H/C) was low at the film surface and rose to a constant value at a depth of 50 nm. Hydrogen to carbon ratios measured half the distance through the DLC films presented in this paper using different deposition methods, are shown in Table I.

There is a variation in hydrogen content which depends upon the method used for deposition of the DLC film. The highest H/C ratio (0.91) exists for DLC films made using $CH_4$ in the single beam ion source. By adding the energy of the second ion source (dual beam) this ratio is reduced to 0.62. Thus, the second source removes some of the hydrogen but leaves enough to provide good transmittance in the visible (Ref. 3). The films generated by ion beam sputter deposition from a graphite target contain the least amount of hydrogen (H/C = 0.22). This could explain their relatively poor transmittance in the visible (Refs. 3 and 5). The addition of hydrogen into the vacuum facility during deposition doubled the hydrogen content in these films, made them softer, less erosion resistant, and did not seem to increase their visible transmittance.

From IR spectroscopy, the integrated intensity of the C-H stretching band at about 3.4 μm indicates that the amount of chemically bonded hydrogen is less than the total hydrogen content in the films, thus indicating a measurable amount trapped free $H_2$ content (Ref. 7).

## Film Stress

DL films were deposited on Si and intrinsic stress measurements were made using an Ionic System's intrinsic stress gauge. All of the DLC films exhibited a compressive stress which varied depending on the deposition method, hydrocarbon gas, and energy of deposition. Shown in Figs. 6 through 8 are the stress levels of 0.1 μm thick DLC films made using the different ion beam deposition methods. Figure 6 is a plot of compressive stress as a function of

initial H/Ar gas ratio for $CH_4$ and $C_4H_{10}$ gases deposited at 100 eV using a single ion source. The stress for each type of film ($CH_4$ or $C_4H_{10}$) is independent of initial hydrogen gas condition, but is 2.5 times as big for $C_4H_{10}$ as it is for $CH_4$. Figure 7 shows that the stress in the $CH_4$ single beam films can be reduced to values as low as $4x10^9$ dyne/cm$^2$ by decreasing the deposition energy to 90 eV. Shown in Fig. 8 is the compressive stress for DLC films made by sputter deposition from a carbon target which includes those DLC films made with the addition of hydrogen. The compressive stress is $1.6x10^{10}$ dyne/cm$^2$ for a pure sputter deposited film and shows a slight rise to $2.3x10^{10}$ dyne/cm$^2$ for a film with hydrogen addition. These stress levels are higher than that of single beam deposition of $CH_4$ at 110 eV. Listed in Table I are the stress levels for the various DLC films. The data indicates that the film stress does not depend on the hydrogen content, but on other parameters, such as the deposition technique, hydrocarbon gas and deposition conditions.

## Adherence

The adherence of the DLC films on fused silica was measured following the procedure used by Mirtich (Ref. 10). $CH_4$ films, up to 1 μm thick, deposited using either the single or dual beam systems, were at least as adherent as the maximum measurable adherence (Ref. 10) of the Sebastian Adherence Tester used in the measurement (~$5.5x10^7$ N/m$^2$ or 8000 psi). These films were so adherent that, for some of the films, portions of the fused silica gave way with the film still intact. Films of $C_4H_{10}$ made using the single ion beam began to spall once the thickness reached 0.15 μm and films that were sputter deposited using the graphite target began to spall when 0.20 μm thick, indicating an upper limit in allowable thickness for these films. This was expected, since the stress levels of these two types of DLC films were greater than those made using $CH_4$ in either the dual or single beam.

## CONCLUDING REMARKS

Three different ion beam methods were used to deposit DLC films on fused silica and silicon substrates. Particle erosion tests showed that DLC films generated using $CH_4$ in the dual or single beam ion source system or sputter deposition of a carbon target do protect fused silica and extend erosion lifetime. Hydrogen addition to sputter deposited carbon caused the films to become nonprotecting from sand erosion.

All the films deposited on Si wafers acted as an antireflective coating and resulted in an enhancement of the IR transmittance to varying degrees. DLC films deposited on ZnSe did not change the ZnSe spectral transmittance. Compressive stress exhibited by the DLC films did not depend on hydrogen content, but on other parameters such as the deposition process, hydrocarbon gas used to generate the film and the deposition conditions in the process. Elevated stress levels of films generated using $C_4H_{10}$ or carbon sputter deposition indicate that one may not be able to generate thick films with good adherence on ZnSe or ZnS. The stress of DLC films deposited using $CH_4$ in the single beam ion source showed a strong dependence on deposition energy. Lowering the deposition energy to 90 eV reduced the stress to $4\times10^{-9}$ dyne/cm$^2$, the lowest of any ion beam deposition method.

The use of $CH_4$ in the single beam ion source system appears to be the most attractive method to deposit DLC films on ZnS and ZnSe. This system generated films that had desirable IR transmittance, low stress, and good adherence, in addition to protection from sand erosion.

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TABLE I. - VARIOUS PROPERTIES OF DIAMONDLIKE CARBON FILMS DEPOSITED USING DIFFERENT ION BEAM DEPOSITION METHODS

| Property/ deposition method | Maximum thickness (no spalling), µm | Stress, $dyne/cm^2$ | Percent increase in IR transmittance for a DLC film on Si (0.1 µm) thick | | Hydrogen content, (H/C) ratio |
|---|---|---|---|---|---|
| | | | λ = 5 µm | λ = 10 µm | |
| Dual beam $CH_4$ | >1.5 | $0.9\times10^{10}$ | -- | -- | 0.62 |
| Single beam $CH_4$ | >1.5 | .9 | 2 | 1 | .91 |
| Single beam $CH_4$ | >1.5 | .9 | -- | -- | ---- |
| Single beam $C_4H_{10}$ | .2 | 2.6 | 4 | 0 | .62 |
| Carbon sputtering | .2 | 1.6 | 4 | 2 | .22 |
| Carbon sputtering $+H_2$ addition | --- | 2.3 | 1 | 1 | .53 |

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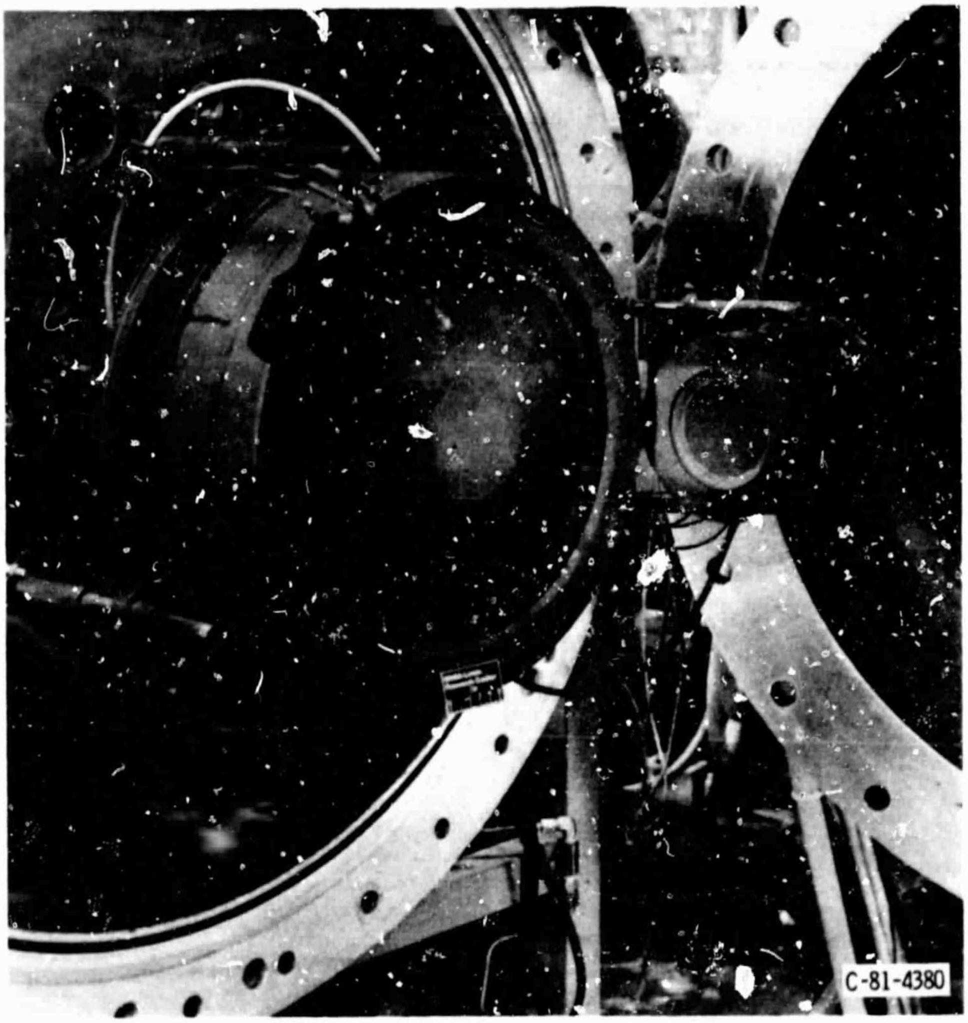


Figure 1. - Dual bea n ion source for deposition of films with diamond like properties.

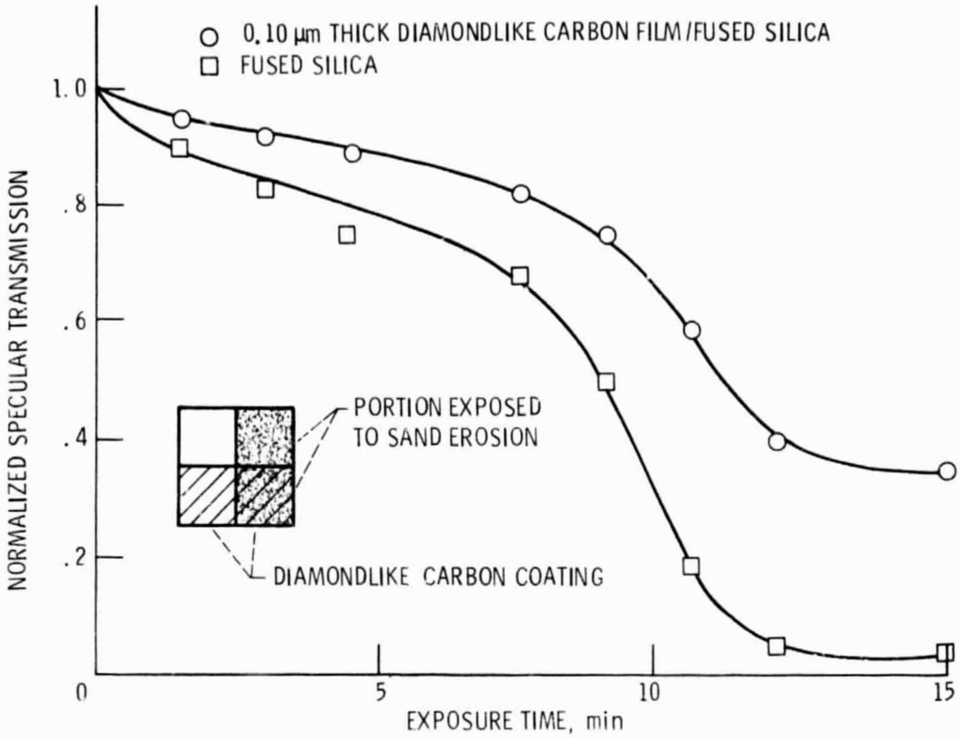


Figure 2. - Comparison of normalized specular transmittance at 0.633 μm of DLC carbon film 0.10 μm thick, deposited using $CH_4$ in a single beam ion source, and fused silica after exposure to 100 μm diameter $SiO_2$ particles at 60 mi/hr.

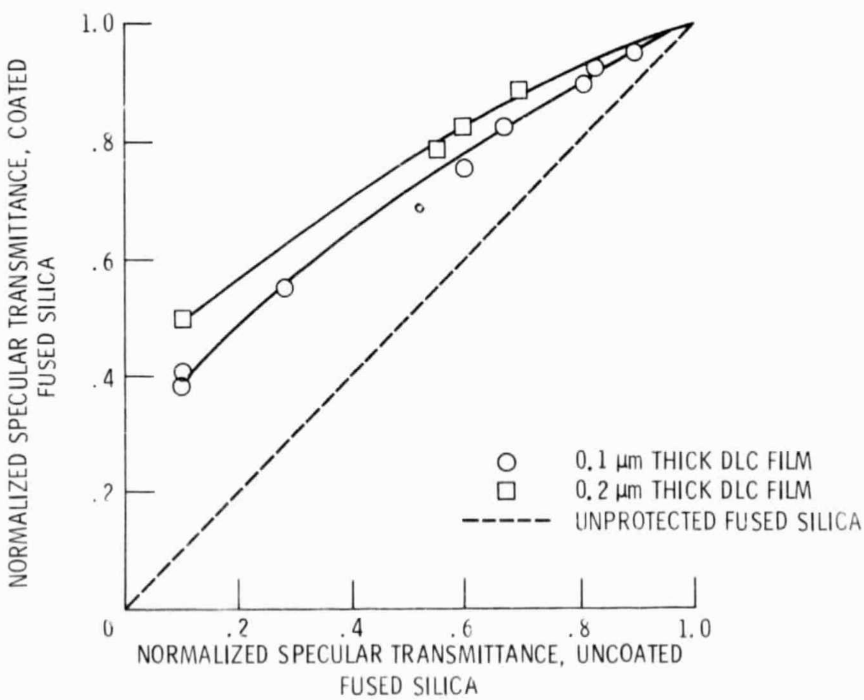


Figure 3. - Normalized specular transmittance of 0.1 μm and 0.2 μm thick DLC films made with $CH_4$ in the single beam ion source vs the normalized specular transmittance of uncoated fused silica, after exposure to 100 μm $S_iO_2$ particles at 60 mi/hr.

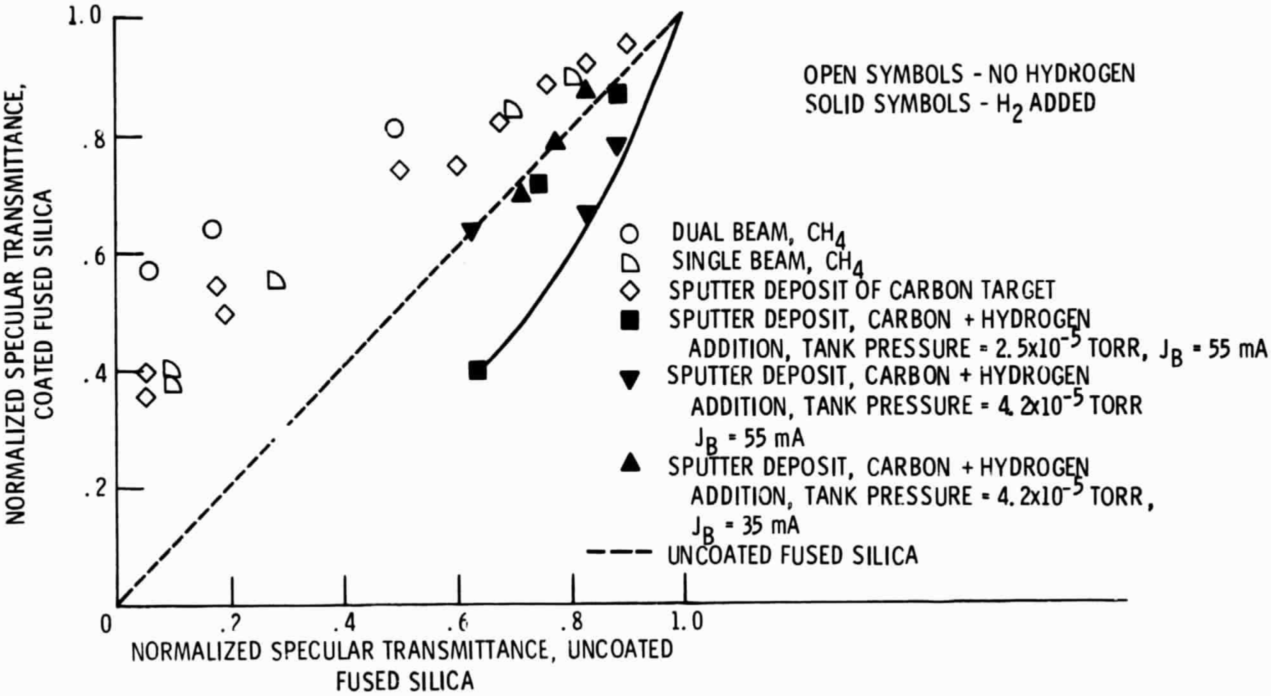


Figure 4. - The effect of 0.1 um thick diamondlike carbon films deposited by various methods on the extension of erosion lifetime, after exposure to 100 μm $SiO_2$ particles at 60 mi/hr.

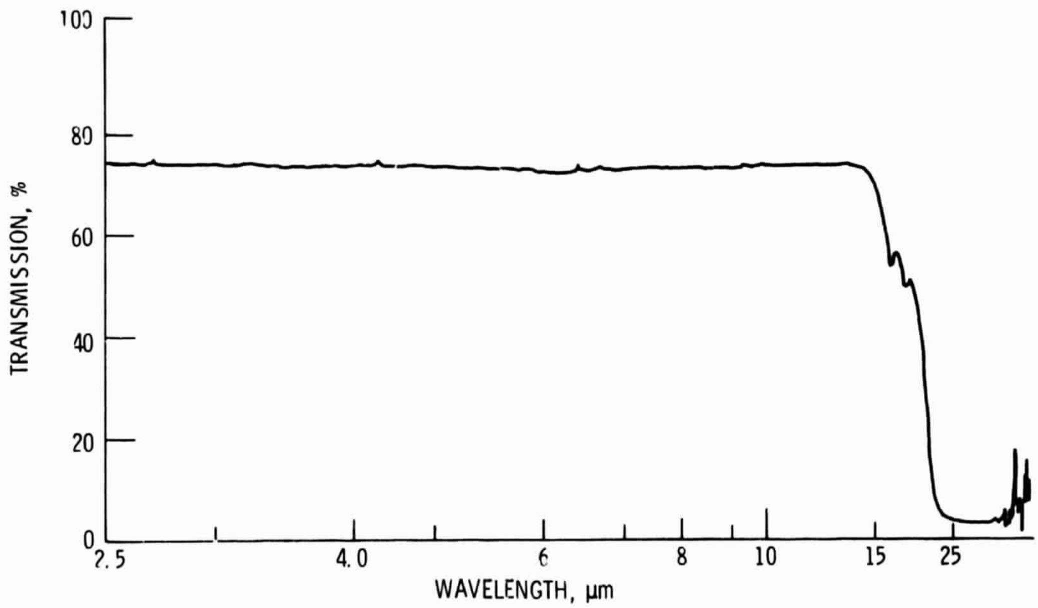


Figure 5. - Infrared transmittance of 0.09 μm thick DLC film deposited on ZnSe, using direct deposition of $CH_4$ in a single beam ion source at 110 eV.

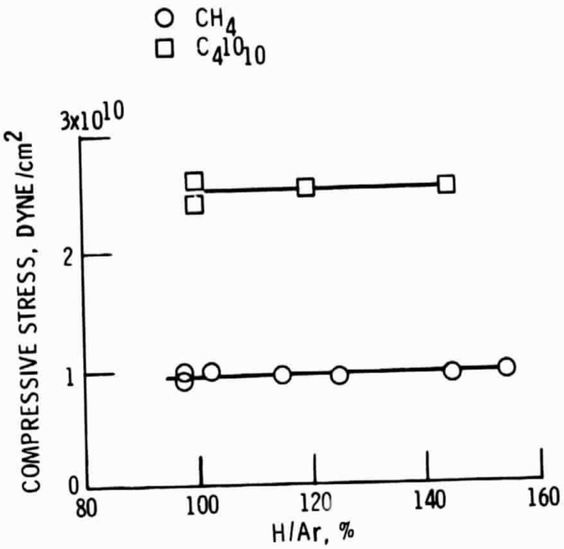


Figure 6.- Stress vs H/Ar ratio for 0.1 μm DLC films made with $CH_4$ and $C_4H_{10}$ in the single beam ion source at 110 eV.

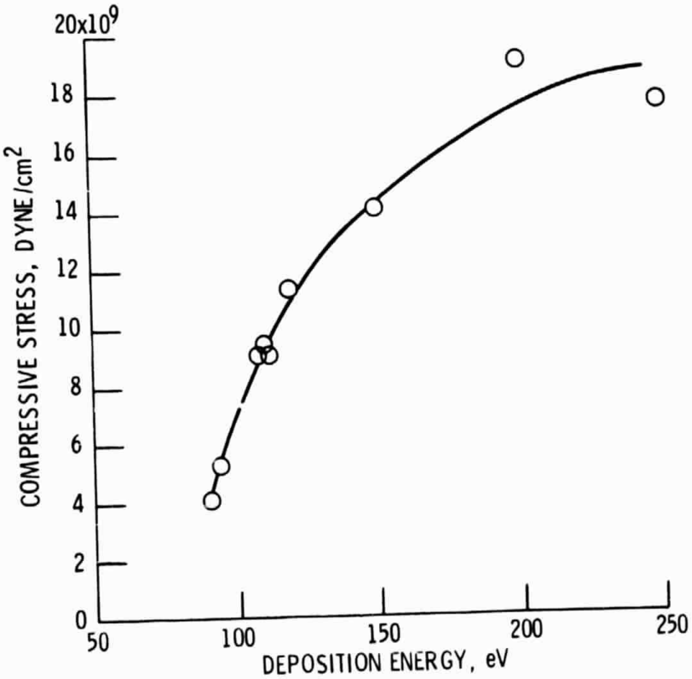


Figure 7. - Stress vs deposition energy for DLC films made with $CH_4$ in the single beam ion source.

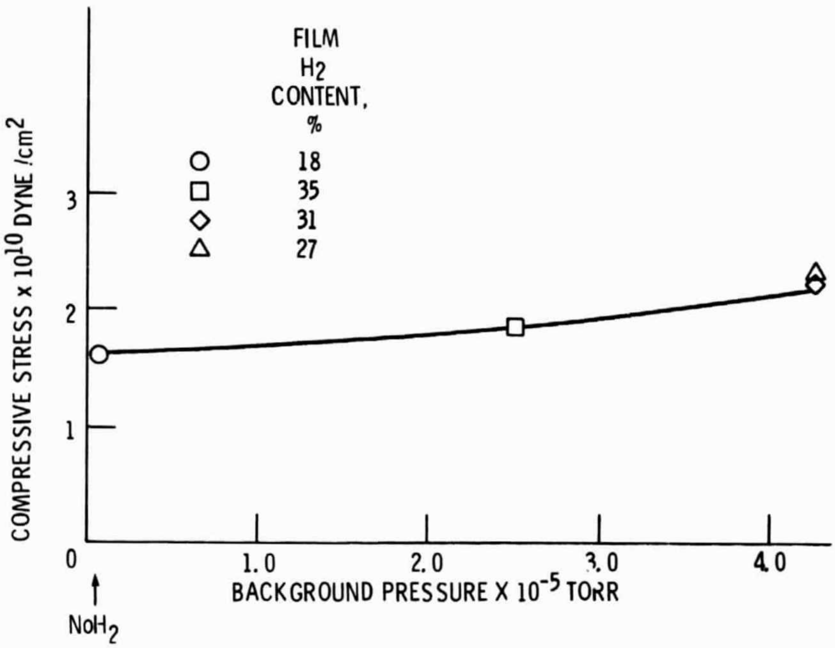


Figure 8. - Stress vs background pressure for DL films made by sputter deposition of a graphite target plus the addition of $H_2$ into the vacuum tank.

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15. Supplementary Notes

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